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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Open-pore polyurethane (OPP) columns are prepared by in-situ polymerization of toluene–carbon tetrachloride solutions of an isocyanate and a polyol. Columns of OPF have been tested for ion-exchange properties, solvent compatibilities, and ability to remove and concentrate polynuclear aromatic hydrocarbons (PAH) from water. Solutions containing 1 μg of pyrene per liter of water have been concentrated 200-fold by passing 1000 mL through a 0.3 × 5 cm column and eluting the pyrene with 5 mL of methanol. Recovery of pyrene was approximately 100%. Results of comparisons of breakthrough capacities and elution rates for PAH on OPP, Amberlite XAD-2, and Bio-Rad AG MP-50 are presented.

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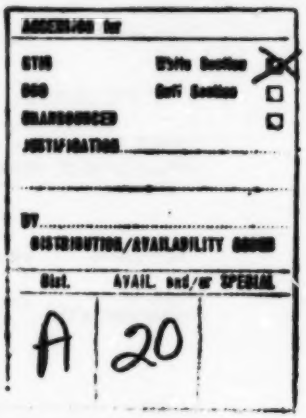


Open-Pore Polyurethane Columns for Collection and Preconcentration of Polynuclear Aromatic Hydrocarbons from Water

James D. Navratil

Rockwell International, Rocky Flats Plant, Golden, Colorado 80401

Robert E. Sievers* and Harold F. Walton

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Open-pore polyurethane (OPP) columns are prepared by in-situ polymerization of toluene–carbon tetrachloride solutions of an isocyanate and a polyol. Columns of OPP have been tested for ion-exchange properties, solvent compatibilities, and ability to remove and concentrate polynuclear aromatic hydrocarbons (PAH) from water. Solutions containing 1 μg of pyrene per liter of water have been concentrated 200-fold by passing 1000 mL through a 0.3 × 5 cm column and eluting the pyrene with 5 mL of methanol. Recovery of pyrene was approximately 100%. Results of comparisons of breakthrough capacities and elution rates for PAH on OPP, Amberlite XAD-2, and Bio-Rad AG MP-50 are presented.

This paper deals with the comparison of in-situ formed open-pore polyurethane (OPP) with other new materials for the removal and concentration of polynuclear aromatic hydrocarbons (PAH) from water. OPP has also been tested for ion-exchange properties, solvent compatibilities, and other characteristics.

OPP is composed of agglomerated spherical particles (1 to 10 μm in diameter) bonded to each other in a rigid, highly permeable structure (*1–4*). We have shown scanning electron micrographs of OPP in a recent publication (*4*). It was first used in a column by Ross and Jefferson in 1970 (*1*). OPP was also used as an efficient gas chromatographic support (*2*) and for liquid chromatography separations with nonaqueous solvents (*3, 4*). No study has been reported, to the best of our knowledge, in which OPP has been used for removing organic compounds from water.

Much work has been reported, however, on the use of cellular (foamed) polyurethane for the collection, separation, and recovery of various inorganic and organic components from aqueous solution (*5*). Polyurethane foam plugs were investigated as a replacement for carbon as a sorbent for preconcentration of organics prior to analysis (*6*) and for removal of organics from wastewater (*7*). Foam plugs were used successfully for the preconcentration of polychlorinated biphenyls (*8–10*) and chlorinated insecticides (*10*) from water. For oil concentration from water, polyurethane gave a lower collection efficiency than liquid–liquid extraction (*11*), and for several organic compounds including naphthalene, polyurethane foams were not as effective as chloroform extraction and Amberlite XAD resin sorption (*12*). Other than naphthalene, sorbtion of PAH on polyurethanes has not been tested.

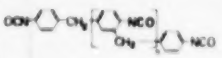
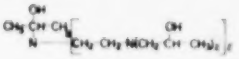
Table I shows the structures of the PAH studied. Carbon adsorption, liquid–liquid extraction, reverse osmosis, and macroreticular resins have been studied for the preconcentration of PAH from water (*7, 13*). The most popular methods have been the use of Amberlite XAD macroreticular resins

Table I. Polycyclic Aromatic Hydrocarbons Studied

Compound	Structure
Benzo [a] pyrene (Aldrich, 96%)	
Biphenyl	
Fluoranthene (Aldrich, 98%)	
Naphthalene (Baker, reagent)	
Phenanthrene (Matheson, technical[a])	
Pyrene (K&K, reagent[a])	

[a] Purified further by sublimation.

Table II. Materials and Reaction for Preparation of Open-Pore Polyurethane of Various Compositions

Trade Name	Structure	Grams of Material per 25 ml Solvent OH/NCO=1.0	OH/NCO=2.2
Mondur MR (Mobay Chemical Co.)		3.16	2.00
LA-475 (Union Carbide Corp.)		2.84	4.00

Reaction:

(*14*), Tenax GC (a polymer of phenylene oxide) (*15*, *16*), and ion exchange resins (*17*).

Several general analytical techniques have been used with the popular preconcentration methods. After the water sample is passed through the sorbent material, the PAH are stripped from the sorbent material two different ways. Either the PAH are removed with a small volume of solvent (*14*) or the PAH are thermally desorbed directly into a gas chromatograph–mass spectrograph (GC-MS) (*18*, *19*). The stripping solvent containing the PAH can be analyzed by ultraviolet (UV) spectrophotometry or the sample concentrated and injected into a GC-MS. Other techniques under investigation include liquid chromatography (LC) (*17*).

We have been exploring the use of OPP for LC. It is envisioned that a small OPP column could be used to concentrate the PAH, then used as a precolumn in LC, or the PAH could be stripped with a small volume of solvent and injected into a GC-MS. Another objective was to compare OPP to some of the popular sorbent materials for the preconcentration of PAH from water.

EXPERIMENTAL

Table II shows the materials for OPP preparation. The OPP columns were prepared by in-situ polymerization of 60–40 vol % toluene–carbon tetrachloride solutions of an isocyanate and a polyol (*4*). The isocyanate is a mixture of 4,4′-diphenylmethane–diisocyanate with lesser amounts of the tri-, tetra-, and pentaisocyanates, and the polyol was principally a pentahydroxy compound resulting from the total oxypropylation of diethylenetriamine. OPP made from monomer formulations with OH–NCO ratios of 1.0 and 2.2 was prepared in glass columns (5 or 10 cm in length and 3.2 mm in diameter). The reaction mode involves the addition of a hydroxy group to an isocyanate to yield a substituted amide ester of carbonic acid (polyurethane). The density of the OPP formed was 0.197 g/mL. Three different batches of Mondur MR were employed for the syntheses. No appreciable differences were observed in the properties of the columns prepared from different lots of the isocyanate.

Table III. Compatibility of OPP with Various Solvents

Solvent	Maximum pump pressure, lb/in.^{2}[a]	Weight loss, %[b]
Acetone	330 ± 10	...
Heptane	>330	−1.2
Ethanol	>330	−1.2
Methanol	>330	−1.2
1 M HCl	175 ± 5	−7.6
1 M HNO_3	330 ± 10	+1.2
1 M H_2SO_4	113 ± 47	...
H_2O	250 ± 12	−2.5
0.1 M NH_3	15 ± 5	...
1 M NH_3	85 ± 15	−3.5
1 M NaOH	<10	−1.1

[a] Pressure to break the OPP to glass column bond after storage of OPP columns (5 cm long) in solvent for 1 week. [b] After passage of 1 L of solvent through OPP column 10 cm long.

Prior to use, the OPP columns were rinsed with 100 mL of heptane, 20 mL of methanol, and 10 mL of deionized-distilled water.

For breakthrough studies the aqueous pyrene solutions were prepared in volumetric flasks by dilution of a stock methanol solution with water. The stock solution containing 9 μg/mL pyrene in methanol was pipetted into a flask partially filled with water by placing the pipet tip under the water surface. The flask was then filled to volume with water and shaken. The aqueous solutions were used immediately because they are not stable over long periods of time.

RESULTS AND DISCUSSION

Compatibility of Solvents with OPP. Compatibilities of OPP with various solvents were determined by checking the strength of the OPP to glass column bond and the weight loss of OPP. The first method consisted of storing columns (5 cm long) of OPP (monomer OH/NCO = 2.2) in the solvents for 1 week. Then, one end of the column was connected to a stainless steel cylinder pump (500-mL volume) with Chem-inert fittings and tubing (Chromatronix). The pump containing water was pressurized with nitrogen from 0 to 330 lb/in.^{2} in 5 lb/in.^{2} increments. The pressure at which the cylinder of dislodged OPP came out the open end of the glass column is given in Table III. The error limits are the standard deviations between three different tests with OPP prepared on different occasions.

The other method consisted of passing 1 L of solvent from the cylinder pump through a dried, tared OPP column (10 cm long) under low pressure (50 lb/in.^{2}). Afterwards the OPP was dried, weighed, and the weight difference divided by the initial weight of the OPP was taken as the weight loss ratio.

The results of the compatibility tests (Table III) show that the OPP (OH/NCO = 2.2) is compatible with organic solvents, water, and dilute acids. However, bases appeared to break the OPP to glass column bond easily.

OPP (OH/NCO = 2.2) columns used routinely for the preconcentration of PAH had a limited life. Passing large volumes of water (a total of 12–24 L) through the 5-cm columns at 50-100 lb/in.^{2} pressure eventually broke the OPP-column bond (over a period of several weeks). Etching the inside of the glass columns with hydrofluoric acid prior to formation of OPP appeared to increase the useful life of

Table IV. Distribution Coefficients for OPP

Material	K_D (Ca^{2+})	K_D ($CdCl_4^{2-}$)
OPP (OH/NCO = 1.0)	<0.1	7 ± 2
OPP (OH/NCO = 2.2)	<0.1	64 ± 6
Dowex 50	150 ± 15	...
Dowex 1	...	700 ± 70

the OPP columns. Perhaps the life of the OPP columns could also be lengthened by lowering the pH of the water samples.

Ion-Exchange Properties of OPP. Batch equilibrium tests were performed to determine the distribution coefficients of several anions and cations with OPP. Dried 1.0-g batches of OPP, Dowex 50, and Dowex 1 were weighed and mixed with 1 M HCl solutions (25 mL) of calcium (1.0 g/L) and cadmium (1.1 g/L) in sealed polyethylene bottles. The batches were stirred for 12 and 15 days. After the mixing period, the solutions were filtered through Whatman No. 42 filter paper. The metal ion concentrations in the solutions were determined by atomic absorption before and after equilibration with the various polymers.

The results shown in Table IV are an average of equilibration for the two different times, and indicate that both formulations of OPP have no cation-exchange properties, but indeed have anion-exchange properties. The latter result is not surprising since one might expect that OPP would be a weak base anion-exchanger from examining its structure.

The anion-exchange capacity was also determined. The determination involved passing 100 mL of 2 M HCl through a column (10 cm long) of OPP (OH/NCO = 2.2), then 25 mL H_2O, and finally 50 mL of 1 M NaOH. The sodium hydroxide solution was analyzed for chloride. Duplicate experiments showed the chloride capacity of OPP to be about 1.2 mequiv/g.

Preconcentration of PAH from Water. OPP (OH/NCO = 1.0 and 2.2) was compared to Amberlite XAD-2 (20–50 mesh macroreticular beads, Polysciences, Inc.) and Bio-Rad AG MP-50 (Ca^{2+} form, 100–200 mesh macroreticular beads, Bio-Rad Laboratories) for PAH breakthrough capacity and elution behavior. The recovery efficiency was also determined for the PAH on OPP.

Pyrene Breakthrough. In a comparison of the capacity of the three materials, solutions of pyrene (0.9 μg/mL) were passed through columns (5 cm long) of all four materials at various flow rates, and fractions were analyzed by UV spectrophotometry on a Cary 14 or Cary 17 spectrophotometer using 10-cm cells. The absorbance peak of pyrene at 335 nm was used for the measurements.

The results of the breakthrough capacities of the materials are shown in Figure 1. C/C_0 is defined as the concentration of pyrene in the column effluent divided by the pyrene concentration in the influent (0.9 μg/mL). Breakthrough capacity is defined for present purposes as the weight of the test substance that can be sorbed by the polymer before C/C_0 becomes greater than 0.1. When less than 90% of the compound in the incoming stream is being sorbed, the polymer is judged to be no longer effective as a collection medium. The data show that OPP with OH/NCO = 1.0 had a much lower capacity than OPP with OH/NCO = 2.2. The latter OPP formulation had the highest breakthrough capacity, followed by Bio-Rad AG MP-50. Amberlite XAD-2 had a fairly low breakthrough capacity. As expected, the breakthrough capacity increases as the flow rates are decreased.

Pyrene Elution. The volume of organic solvent required to quantitatively elute pyrene from the four materials was determined. Anhydrous methanol (Mallinckrodt, Analytical Reagent) or anhydrous ethanol (J. T. Baker, reagent grade) was pumped at 1 mL/min through 5-cm columns of the materials, previously loaded with 5 μg of pyrene (dissolved in water). The effluent stream was passed through a

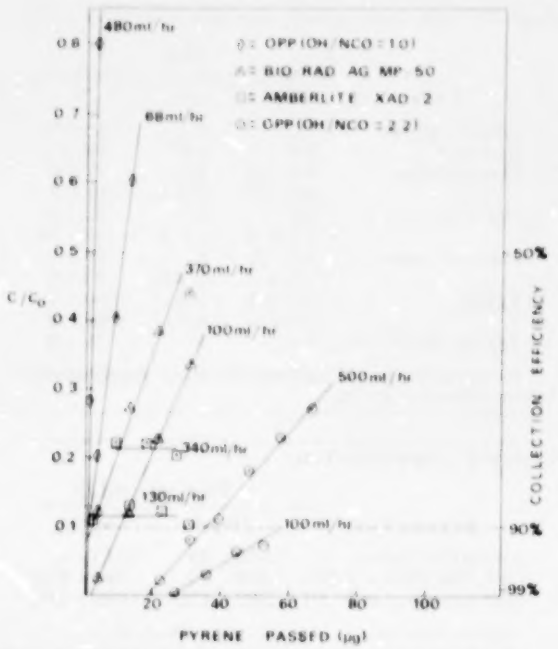


Figure 1. Breakthrough results for pyrene on various polymers

Table V. Volumes of Methanol and Ethanol Required to Elute Pyrene from Various Polymers[a]

Material	MeOH, mL	EtOH, mL
OPP (OH/NCO = 2.2)	2.0 ± 0.6	1.4 ± 0.2
OPP (OH/NCO = 1.0)	2.3 ± 0.5	...
Bio-Rad AG MP-50	3.4 ± 0.6	...
Amberlite XAD-2	5.9 ± 1.2	5.4 ± 1.4

[a] Columns 5 cm long, loaded with 5 μg of pyrene.

Chromatronix Model 220 (254 nm) detector and the pyrene peak was recorded on a dual input Omniscribe recorder (Houston Instrument Corp.). The solvent volume required to quantitatively elute the pyrene (>99% recovery) was determined 3 to 5 times for each material.

The results, shown in Table V, are the average values and the standard deviations of the elution volumes. The results show little significant difference between the two different formulations of OPP and between methanol and ethanol eluent. The OPP allowed faster elution of pyrene with smaller volumes of eluent than did Bio-Rad AG MP-50 and Amberlite XAD-2.

Recovery of PAH. Synthetic samples of PAH were prepared freshly each day by diluting 1–5 mL of stock PAH solution in methanol to 2 L of deionized-distilled water. The PAH solutions were then placed in the cylinder pump (50–100 lb/in.^{2} N_2) and passed through 5-cm columns of OPP (or, in one case, Amberlite XAD-2). After 1 L of the solution was passed through the column, the PAH were eluted from the column with methanol. Two, and sometimes three, 5-mL volumetric flasks of eluate were collected and the concentration of PAH was determined by UV spectrophotometry. For each of the PAH, 3 to 5 recovery determinations were performed.

The average and standard deviation of the determinations are shown in Table VI. The results show that excellent recovery of PAH was achieved using OPP under a variety of conditions. Fluoranthene, naphthalene, and phenanthrene had good recovery when the capacity of the OPP for these PAH was not reached (~3 μg). Pyrene recovery from Amberlite XAD-2 was not as good as OPP, which is in agreement

Table VI. Recovery of PAH with OPP (OH/NCO = 2.2)

PAH	Flow rate, L/h	PAH Loaded, μg	Recovery, %
Benzo[*a*]pyrene	1.8	4	95 ± 6
Biphenyl	0.9-1.5	5-6	98 ± 5
Fluoranthene	0.5-1.0	4-5	77 ± 4
	0.5-1.0	1-2.5	97 ± 3
Naphthalene[a]	0.1	5	56 ± 3
	0.1-1.0	1-2.5	98 ± 10
Phenanthrene	0.8-1.0	5	58 ± 7
	0.8-1.0	1-2.5	92 ± 9
Pyrene	0.6-0.8	1-4	100 ± 2
	1.2-1.7	4-5	89 ± 3
Pyrene (XAD-2)[a]	0.6	4	79 ± 8

[a] Required 10 mL of methanol to elute quantitatively; others needed only 5 mL.

Table VII. Flow Rate Tests

Material, 5 cm	Flow rate, mL/h 10 psi	50 psi
Amberlite XAD-2	360 ± 24	1040 ± 0
OPP (OH/NCO = 2.2)[a]	230 ± 80	780 ± 200
OPP (prepared at 0 °C)	560 ± 220	1670 ± 490

[a] Gravity flow rate = 10 mL/h with 10-cm head.

with the breakthrough capacity results.

A second 5-mL fraction of methanol was required to quantitatively elute (>99%) naphthalene from OPP and pyrene from XAD-2. The remainder of the PAH were eluted with 5 mL of methanol.

Possible Interferences in UV Determinations of PAH. Humic substances could interfere with the UV determination of PAH in actual water samples if they sorb on OPP and then are subsequently eluted by methanol. To check the retention and UV interference of humic substances, the water used to make up the synthetic pyrene solutions was boiled for 1 h in the presence of peat moss and filtered with Whatman No. 1 filter paper. The pyrene solution containing humic and fulvic acids was then concentrated in the same manner as in the recovery experiments. The methanol eluate gave an identical spectrum, with no additional baseline noise, to that of a solution containing no humic substances. This showed that the humic substances would not interfere with the UV determination of PAH after preconcentration on OPP. Either the humic acids are not sorbed or they are not eluted by methanol to cause interference in measurements with UV detectors.

Pressure Drop. One apparent disadvantage of the OPP in comparison to Amberlite XAD-2 is the additional pressure drop across a 5-cm column. Table VII shows the flow rates at two different cylinder pump pressures of water through the materials. The flow rates are an average of 6 different tests. The results show that OPP prepared at 0 °C instead of 23–25 °C gave a higher flow rate, even better than XAD-2. This is believed to be due to the larger microspherules formed at 0 °C relative to those synthesized at higher temperatures. The recovery of pyrene was not significantly different with the OPP prepared at 0 °C as compared to the room temperature OPP preparation.

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